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Empirical Approach to Phase Equilibrium Behavior of Quasi-Binary Polymer Solutions

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ABSTRACT: A simple expression was derived for the Gibbs free energy G of the binary system consisting of monodisperse polystyrene (PS) and cyclohexane (CH) from previously reported light scattering data. By some ad hoc assumptions it was modified to the G function of a system containing two monodisperse PS in CH. No additional parameter was introduced in making this modification. The binodals, cloud-point curves, and critical points calculated with the G function so obtained were found to agree almost quantitatively and consistently with the experimental data of two quasi-binary systems A and B: in A, the polymer is a mixture of PS samples f4 ($M_w = 45\,300$) and f40 ($M_w = 498\,000$), and in B, it is a mixture of PS samples f4 and f10 ($M_w = 103\,000$).

One of the unsolved problems of polymer physical chemistry is the quantitative prediction of phase relationships in macromolecular solutions. Our recent formulation of the Flory–Huggins interaction parameter χ on the basis of light scattering data has made it possible to predict accurately cloud points, spinodal points, and critical points of the binary system consisting of monodisperse polystyrene (PS) and cyclohexane (CH).[1] However, a similar formulation for quasi-binary systems, i.e., solutions containing two or more monodisperse homologous polymers in a pure solvent is considerably more difficult, since a vast amount of light scattering data must be obtained by varying the composition of the polymer mixture as well as the molecular weights of its constituent polymers.

In this paper, we propose another empirical approach to the phase equilibrium behavior of quasi-binary systems. The basic idea is to adapt, by some ad hoc assumptions, the free energy function of a binary system to that of such systems. The assumptions used are tested by comparing their consequences with the experimental data[2,3] previously reported from our laboratory.

Strictly Binary System

Basic Equations. We consider a strictly binary system, made up by dissolving a monodisperse (homo)polymer (component 1) in a pure solvent (component 0). The ratio of the molar volume of component 1, V_1, to that of component 0, V_0, is denoted by P and referred to as the relative chain length of the polymer. As the concentration variable, we adopt a quantity ϕ defined by

$$\phi = n_1V_1/(n_0V_0 + n_1V_1) = n_1P/(n_0 + n_1P) \qquad (1)$$

where n_i is the amount in moles of component i and ϕ is the volume fraction of the polymer.

For the reason mentioned below, we formulate the thermodynamic behavior of this system in terms of the difference from that of a hypothetical reference solution in which the chemical potential of the solvent, μ_0^{v}, is given over the entire range of ϕ by

$$\mu_0^{\mathrm{v}} = \mu_0^\circ - (RT/P)\phi \qquad (2)$$

where μ_0° is the chemical potential of the solvent in the pure state and RT has the usual meaning. The chemical potential of component 0, μ_0, in the binary system under consideration may then be represented by

$$\mu_0 = \mu_0^\circ - (RT/P)\phi - \Gamma(T,\phi;P)\phi^2 \qquad (3)$$

where $\Gamma(T,\phi;P)$ is an apparent second virial coefficient to be determined by experiment and is related to the Flory–Huggins interaction parameter χ by

$$\Gamma = -\chi - [\ln(1-\phi) + \phi]\phi^{-2} \qquad (4)$$

Since Γ is small in poor solvent systems, this relation indicates that χ for such a system contains a large contribution, substantially compensating the second term on the right-hand side ($-[\ln(1-\phi) + \phi]\phi^{-2}$) which is of the order of unity and associated with the entropy of the Flory–Huggins athermal solution. Thus, it does not seem advantageous for the formulation of thermodynamic behavior below the Θ temperature to adopt the traditional χ method in which the Flory–Huggins athermal solution is chosen as the reference state.

The Gibbs–Duhem relation gives

$$[(1-\phi)/V_0](\partial\mu_0/\partial\phi) + (\phi/V_1)(\partial\mu_1/\partial\phi) = 0 \qquad (5)$$

where μ_1 is the chemical potential of component 1. Substitution of eq 3 into eq 5, followed by integration, yields

$$\mu_1 = \mu_1^\infty + RT\left[\ln\phi - \phi + \Gamma P\phi(1-\phi) + P\int_0^\phi \Gamma\,\mathrm{d}u\right] \qquad (6)$$

where u is an integration variable and μ_1^∞ is defined by

$$\mu_1^\infty = \lim_{\phi\to 0}(\mu_1 - RT\ln\phi) \qquad (7)$$

The G function of the system under consideration is represented by

$$G = n_0\mu_0 + n_1\mu_1 \qquad (8)$$

Substitution of eq 3 and 6 gives

$$G = (n_0 + n_1P)\left\{(1-\phi)\mu_0^\circ + \phi\mu_1^\infty P^{-1} + RT\left[-\phi P^{-1} + P^{-1}\phi\ln\phi + \phi\int_0^\phi \Gamma\,\mathrm{d}u\right]\right\} \qquad (9)$$

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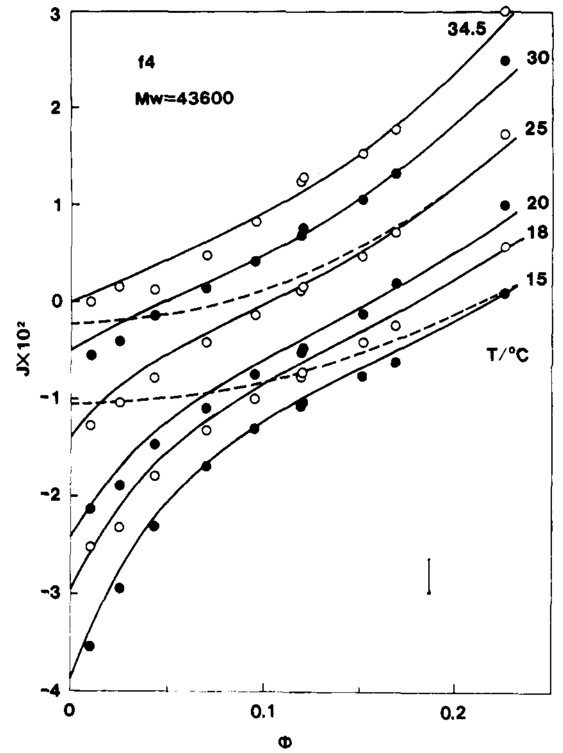

Figure 1. Plots of J vs. ϕ for sample f4 in cyclohexane at the temperatures indicated: circles, experimental; solid lines, calculated J; dashed lines, calculated J_{conc}.

Analysis of Light Scattering Data. In our previous paper[1] we introduced a quantity Z defined by

$$Z = [1/(1 - \phi) + 1/(P\phi) - K/\Delta R_0]/2 \tag{10}$$

where ΔR_0 is the excess Rayleigh ratio at the zero scattering angle and K an optical parameter. According to light scattering theory, it can be shown for strictly binary solutions that Γ is related to Z by

$$J = -Z + 1/[2(1 - \phi)] \tag{11}$$

where

$$J = \Gamma + (1/2)(\partial\Gamma/\partial\phi)\phi \tag{12}$$

Since Z consists of experimentally measurable quantities, it follows from eq 11 that J is obtainable experimentally as a function of ϕ, T, and P.

Figure 1 illustrates plots of J vs. ϕ at several T derived from light scattering data[1] on a PS sample f4 (M_w = 43 600) in CH. The data for samples f20 (M_w = 200 000) and f40 (M_w = 498 000) in CH give J vs. ϕ plots with similar patterns (see Figures 2 and 3).

To describe these plots mathematically, the same strategy is used as that employed for Z in our previous paper.[1] Thus, J is represented as

$$J = J_{\mathrm{conc}} + (J_{\mathrm{dil}} - J_{\mathrm{conc}})Q \tag{13}$$

and the factor multiplied by Q is approximated with its infinite-dilution value $J_{\mathrm{dil}}^{\circ} - J_{\mathrm{conc}}^{\circ}$. Here, J_{dil} and J_{conc} are the J functions characterizing dilute and concentrated solutions, respectively, and Q the probability that a small volume element in the solution is not occupied by any polymer segment.

After some trials the following simple expressions were chosen for J_{conc} and Q:

$$J_{\mathrm{conc}} = J_{c0} + J_{c1}\phi^2 \tag{14}$$

$$Q = \exp(-\phi/b) \tag{15}$$

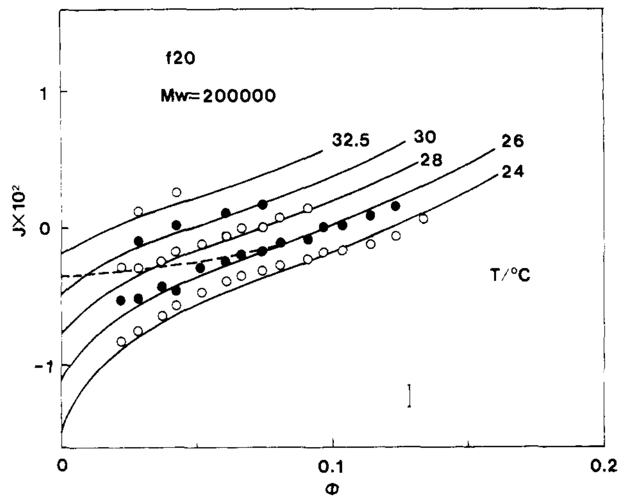

Figure 2. Plots of J vs. ϕ for sample f20 in cyclohexane at the temperatures indicated: circles, experimental; solid lines, calculated J; dashed line, calculated J_{conc}.

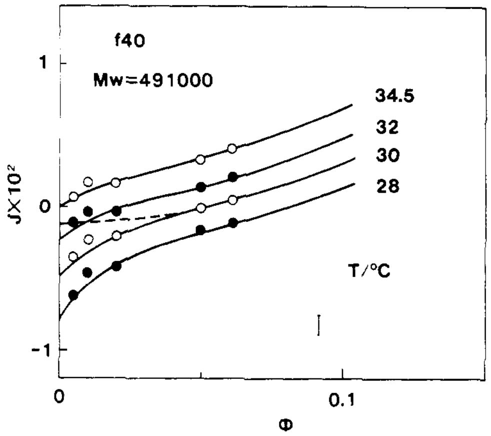

Figure 3. Plots of J vs. ϕ for sample f40 in cyclohexane at the temperatures indicated: circles, experimental; solid lines, calculated J; dashed line, calculated J_{conc}.

With these and the approximation stated above, eq 13 can be written

$$J = J_{c0} + J_{c1}\phi^2 + (J_{\mathrm{dil}}^{\circ} - J_{c0}) \exp(-\phi/b) \tag{16}$$

Among the four parameters J_{c0}, J_{c1}, J_{dil}°, and b to be determined as functions of T and P from experimental data, J_{dil}° was obtained from our previous light scattering data[1] in the following way. Equation 16 gives

$$\lim_{\phi \to 0} J = J_{\mathrm{dil}}^{\circ} \tag{17}$$

As shown previously,[1] Z for a binary solution is related to χ by

$$Z = \chi + (1/2)(\partial\chi/\partial\phi)\phi \tag{18}$$

which is combined with eq 11 and 17 to yield

$$J_{\mathrm{dil}}^{\circ} = 1/2 - \chi^{\circ} \tag{19}$$

where χ° denotes the infinite-dilution value of χ, i.e., $\chi_{\mathrm{dil}}^{\circ}$ in our previous paper.[1] With the empirical equation for $\chi_{\mathrm{dil}}^{\circ}$ established for PS in CH, eq 19 gives

$$J_{\mathrm{dil}}^{\circ} = -0.26(\Theta/T - 1) - 4.6(\Theta/T - 1)^2 \tag{20}$$

where Θ denotes the theta temperature for the system PS + CH and is taken to be 307.65 K in the subsequent computations.

In analogy with the treatment of Koningsveld et al.,[4] we considered the parameter b to represent the value of ϕ that just agrees with the volume fraction of segments in the domain occupied by a single polymer molecule and set $b = cP^{-1/2}$, with c being a parameter independent of P.

Trial-and-error fitting of eq 16 to the J vs. ϕ plots for the three PS samples mentioned above, with eq 20 for $J_{\mathrm{dil}}{}^{\circ}$ and $b = cP^{-1/2}$, resulted in the following empirical equations:

$$J_{c0} = 0.036P^{-1/3} - 0.23(\Theta/T - 1) \tag{21}$$

$$J_{c1} = 0.47 - 3.5(\Theta/T - 1) \tag{22}$$

$$b = P^{-1/2} \qquad \text{(i.e., } c = 1\text{)} \tag{23}$$

The solid lines in Figures 1–3 show the J vs. ϕ relations computed from eq 16 with eq 20 through 23. Their fit to the data points is generally satisfactory considering the simplicity of eq 16 as well as the inaccuracy involved in experimentally evaluating J, which is indicated by error bars in the figures. It is important to note that the concentrated solution part of J, i.e., $J_{c0} + J_{c1}\phi^2$, depends on P through the term J_{c0}. This may be compared with our previous finding that the concentrated solution part of χ must be P-dependent. Independently, Nies et al.[5] have drawn a similar conclusion from their approach, which was formulated in terms of the so-called g function (see eq 51).

Cloud-Point Curves. Solution of eq 12 for Γ gives

$$\Gamma = (2/\phi^2)\int_0^{\phi} J\phi \, du \tag{24}$$

which, on substituting eq 16, yields

$$\Gamma = J_{c0} + (1/2)J_{c1}\phi^2 + 2(J_{\mathrm{dil}}{}^{\circ} - J_{c0})b^2[1 - e^{-\phi/b}(1 + \phi/b)]/\phi^2 \tag{25}$$

Equations 3 and 6 with Γ given by eq 25 were substituted into the phase-equilibrium relations for components 0 and 1 to calculate binodals (cloud-point curves for strictly binary solutions). In Figure 4, the calculated cloud-point curves (solid lines) are compared with typical experimental data. Their fit to the plotted points is somewhat inferior to that obtained previously[1] with a G function more complicated than the one derived above. However, we did not attempt a better fit by adding more terms to eq 16 for J.

Simplest Quasi-Binary System

Basic Equations. The simplest of the quasi-binary systems consists of two monodisperse homologous polymers 1 and 2 dissolved in a pure solvent 0. The relative chain length and volume fraction of polymer i ($i = 1, 2$) are denoted by P_i and ϕ_i, respectively. The total volume fraction ϕ of the mixture of polymers 1 and 2 is represented by

$$\phi = \phi_1 + \phi_2 \tag{26}$$

The relevant extension of eq 3 to this quasi-binary system is

$$\mu_0 = \mu_0{}^{\circ} - (RT/P_{\mathrm{n}})\phi - RT\Gamma(T,\phi_1,\phi_2;P_1,P_2)\phi^2 \tag{27}$$

where $\Gamma(T,\phi_1,\phi_2;P_1,P_2)$ is a characteristic function of the system to be determined by experiment and P_{n} denotes the number-average relative chain length of the polymer mixture, which can be represented by

$$P_{\mathrm{n}}{}^{-1} = (\phi_1 P_1{}^{-1} + \phi_2 P_2{}^{-1})/\phi \tag{28}$$

The Gibbs–Duhem relation for the present system gives

$$[(1 - \phi)/V_0](\partial\mu_0/\partial\phi_1) + (\phi_1/V_1)(\partial\mu_1/\partial\phi_1) + (\phi_2/V_2)(\partial\mu_2/\partial\phi_1) = 0 \tag{29}$$

$$[(1 - \phi)/V_0](\partial\mu_0/\partial\phi_2) + (\phi_1/V_1)(\partial\mu_1/\partial\phi_2) + (\phi_2/V_2)(\partial\mu_2/\partial\phi_2) = 0 \tag{30}$$

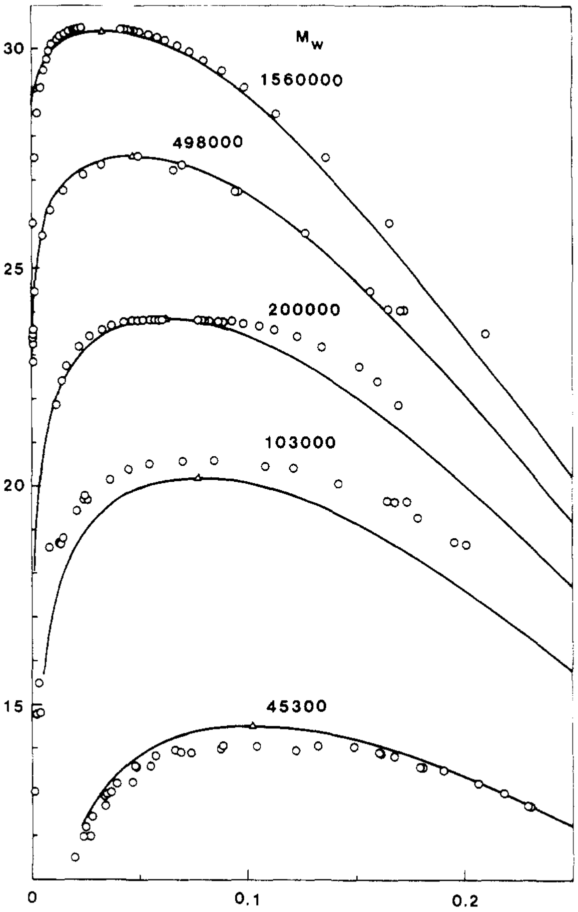

Figure 4. Cloud-point curves (binodals) for narrow-distribution polystyrene in cyclohexane. Molecular weights of the samples are 1 560 000 (Nakata et al.[6]), 498 000 (Tsuyumoto et al.[2]), 200 000 (Nakata et al.[7]), 103 000 (Hashizume et al.[3]), and 45 300 (Hashizume et al.[3]) from top to bottom. Solid lines and triangles are calculated binodals and critical points, respectively.

where μ_i and V_i are the chemical potential and molar volume of component i, respectively; note that $P_1 = V_1/V_0$ and $P_2 = V_2/V_0$. As the composition variables we may use, instead of ϕ_1 and ϕ_2, the total polymer volume fraction ϕ and the volume fraction ξ of polymer 1 in the polymer mixture. The latter is expressed by

$$\xi = \phi_1/(\phi_1 + \phi_2) \tag{31}$$

After rewriting eq 29 and 30 in terms of ϕ and ξ, we can derive by simple operations

$$(1 - \phi)(\partial\mu_0/\partial\phi) + (\phi\xi/P_1)(\partial\mu_1/\partial\phi) + [\phi(1 - \xi)/P_2](\partial\mu_2/\partial\phi) = 0 \tag{32}$$

$$(1 - \phi)(\partial\mu_0/\partial\xi) + (\phi\xi/P_1)(\partial\mu_1/\partial\xi) + [\phi(1 - \xi)/P_2](\partial\mu_2/\partial\xi) = 0 \tag{33}$$

Although the algebraic details are omitted, integration of these differential equations, with eq 27 inserted into μ_0, leads to

$$\mu_1 = \mu_1{}^{\infty} + RT\left\{\ln(\phi\xi) - \phi + (1 - P_1/P_2)(1 - \xi)\phi + \Gamma P_1\phi(1 - \phi) + P_1\int_0^{\phi}[\Gamma + (1 - \xi)(\partial\Gamma/\partial\xi)]\, du\right\} \tag{34}$$

$$\mu_2 = \mu_2{}^{\infty} + RT\left\{\ln[\phi(1 - \xi)] - \phi - (P_2/P_1 - 1)\xi\phi + \Gamma P_2\phi(1 - \phi) + P_2\int_0^{\phi}[\Gamma - \xi(\partial\Gamma/\partial\xi)]\, du\right\} \tag{35}$$

where $\mu_i{}^{\infty}$ is defined by

$$\mu_i{}^{\infty} = \lim_{\phi \to 0}(\mu_i - RT\ln\phi_i) \tag{36}$$

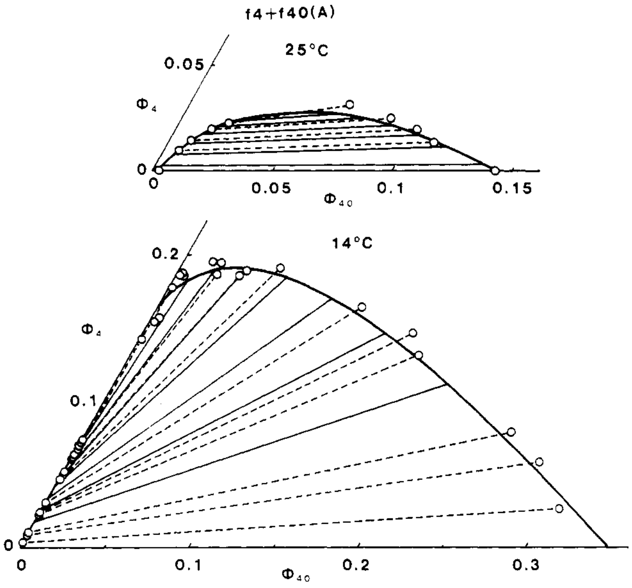

Figure 5. Binodals for system A at 25 °C (upper) and 14 °C (lower): circles, experimental binodals; dashed lines, experimental tie lines; solid curves, calculated binodals; solid straight lines, calculated tie lines.

Substitution of eq 27, 34, and 35 into $G = n_0\mu_0 + n_1\mu_1 + n_2\mu_2$, the Gibbs free energy of the system under study, yields

$$G = (n_0 + n_1P_1 + n_2P_2)\Big\{(1-\phi)\mu_0^\circ + \phi_1\mu_1^\infty/P_1 + \phi_2\mu_2^\infty/P_2 + RT\Big[-\phi/P_n + \phi_1/P_1 \ln \phi_1 + \phi_2/P_2 \ln \phi_2 + \phi\int_0^\phi \Gamma(T,\phi_1,\phi_2;P_1,P_2)\, du\Big]\Big\} \quad (37)$$

Modification of $\Gamma(T,\phi;P)$ to $\Gamma(T,\phi_1,\phi_2;P_1,P_2)$. We propose an empirical approach to $\Gamma(T,\phi_1,\phi_2;P_1,P_2)$. This consists of reinterpreting ϕ in eq 25 for $\Gamma(T,\phi;P)$ as the total polymer volume fraction, replacing P in each of the P-dependent terms (J_{c0} and b) in this equation by a certain mean chain length of the polymer mixture, and regarding the resulting expression as the desired $\Gamma(T,\phi_1,\phi_2;P_1,P_2)$. After many trials we found that the following simple substitutions were promising: (i) P in eq 21 for J_{c0} is replaced by P^* defined as

$$P^* = [\xi P_1^{-1/3} + (1-\xi)P_2^{-1/3}]^{-3} \quad (38)$$

(ii) P in eq 23 for b is replaced by P^{**} defined as

$$P^{**} = [\xi P_1^{-1/2} + (1-\xi)P_2^{-1/2}]^{-2} \quad (39)$$

These are equivalent to assuming that J_{c0} and b of a quasi-binary solution containing polymer 1 and 2 are given by the volume averages of those of the binary solutions, each containing polymer 1 or 2. This assumption is entirely ad hoc, with no theoretical justification at present (see Appendix). However, at least the above substitutions introduce no additional parameter into our formulation.

In the following, typical phase relations are calculated by using $\Gamma(T,\phi_1,\phi_2,P_1,P_2)$ obtained as above and compared with our previously published experimental results[2,3] on two PS + CH systems A and B. Here, the polymer mixture in system A consists of samples f4 and f40 and that in system B of samples f4 and f10 (M_w = 103 000).

Binodals. Figures 5 and 6 compare the calculated and experimental binodals for systems A and B, respectively. It can be seen that for both systems the G function used for the calculations predicts fairly accurately the measured concentrations of the individual polymer components in separated dilute and concentrated phases.

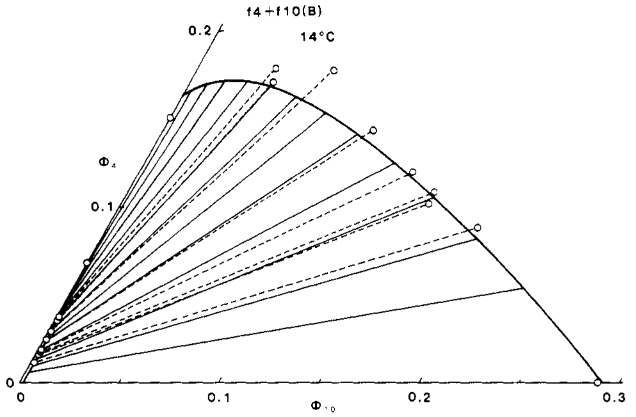

Figure 6. Binodal for system B at 14 °C: circles, experimental binodals; dashed lines, experimental tie lines; solid curve, calculated binodal; solid straight lines, calculated tie lines.

Cloud-Point Curves. The upper panels in Figures 7 and 8 show the calculated cloud-point curves (or coexistence curves) and their conjugate shadow curves at several values of ξ_4, the volume fraction of sample f4 in the polymer mixture, for systems A and B, while the lower panels illustrate the corresponding observed cloud-point curves.[2,3] The dot–dash line in each of the upper panels indicates the locus of the critical points for different ξ_4, which are located at the intersections of cloud-point and shadow curves.

Overall resemblance of the calculated and observed results is apparent at a glance for either system. Especially, in Figure 7, the calculated curves for ξ_4 close to unity exhibit rather sharp breaks in the vicinity of the critical points as do the corresponding observed ones. A detailed comparison reveals some quantitative disagreement between calculated and measured cloud points. As a whole, it is less for system A than for system B. The greatest discrepancy can be seen at $\xi_4 = 0$ in the latter system, but it remains less that 1 °C and seems tolerable for practical purposes.

Critical Points. The critical temperature T_c and concentration ϕ_c for a three-component system can be found by solving the set of relations

$$|G| \equiv G_{11}G_{22} - (G_{12})^2 = 0 \quad (40)$$

$$\begin{vmatrix} \partial|G|/\partial\phi_1 & \partial|G|/\partial\phi_2 \\ G_{21} & G_{22} \end{vmatrix} = 0 \quad (41)$$

where

$$G_{ij} = \partial^2 G/\partial\phi_i\partial\phi_j \quad (42)$$

The values of T_c and ϕ_c calculated and measured for systems A and B are shown in Figures 9 and 10. For either system, the agreement between prediction and experiment is good for T_c but only moderate for ϕ_c; the maximum difference is about 0.5 °C for T_c and about 0.01 for ϕ_c. However, we are content with these results, since, on the one hand, both T_c and ϕ_c are very sensitive to the mathematical structure of the G function (because they depend on the third derivatives of G with respect to composition variables) and, on the other hand, their accurate measurement for quasi-binary solutions is not always easy.

Discussion

Extension to General Quasi-Binary Solutions. From eq 37 it may be inferred that the G function for a general quasi-binary system containing any number N of homologous monodisperse polymers in a single solvent is given by

$$G = (n_0 + \sum_{i=1}^{N} n_i P_i)\Big\{(1 - \phi)\mu_0{}^\circ + \sum_{i=1}^{N} \phi_i \mu_i{}^\infty / P_i + RT\Big[-\phi/P_\mathrm{n} + \sum_{i=1}^{N}(\phi_i/P_i)\ln\phi_i + \phi\int_0^\phi \Gamma(T,\phi_1, ..., \phi_N;P_1, ..., P_N)\,\mathrm{d}u\Big]\Big\} \quad (43)$$

with

$$P_n = [\sum_{i=1}^{N} \xi_i P_i{}^{-1}]^{-1} \quad (44)$$

where ξ_i is the volume fraction of polymer i in the polymer mixture

$$\xi_i = \phi_i/\phi \quad (45)$$

For PS in CH, the empirical substitutions (i) and (ii) may be generalized as follows:

$$P^* = [\sum_{i=1}^{N} \xi_i P_i{}^{-1/3}]^{-3} \quad (46)$$

$$P^{**} = [\sum_{i=1}^{N} \xi_i P_i{}^{-1/2}]^{-2} \quad (47)$$

Work is in progress in our laboratory to check this generalized G function with measurements of σ_i on CH solutions containing four monodisperse PS samples at various compositions.[8] Here, σ_i denotes the separation factor (or the partition coefficient) for polymer i defined as

$$\sigma_i = P_i{}^{-1}\ln(\phi_i''/\phi_i') \quad (48)$$

with ϕ_i' and ϕ_i'' being the volume fractions of polymer i in the equilibrium dilute and concentrated phases, respectively. The results obtained so far are encouraging but have revealed the important fact that our G functions for the binary and quasi-binary systems of PS + CH must be modified when the system contains a polymer species with a molecular weight as low as 10^4.

Approach of Nies et al. Recently, Nies et al.[5] reported an empirical approach to phase separation behavior of polymer solutions, using the so-called g function, which, like χ, absorbs all deviations of actual solutions from the Flory–Huggins athermal solution. As we did for $\Gamma(T,\phi;P)$, they assumed for g a fixed function of ϕ as

$$g = B(T)/(1 - \gamma\phi) + A(T,P) + g^*(T,P)\exp(-\lambda P^{1/2}\phi) \quad (49)$$

but, differing from our approach, they assigned to $B(T)$, $A(T,P)$, and $g^*(T,P)$ the following special forms:

$$B(T) = B_1 + B_2/T \quad (50)$$

$$A(T,P) = A_{10} + A_{11}/P + (A_{20} + A_{21}/P)(T - \Theta) \quad (51)$$

$$g^*(T,P) = [g_1 + g_2(T - \Theta)](T - \Theta)/P \quad (52)$$

The first two terms in eq 49 represent the concentrated solution part of g, and g^* signifies the effect due to the nonuniform segment distribution in dilute solutions.

Nies et al. evaluated all coefficients in the above equations by fitting eq 49 to the data for χ, cloud points, spinodals, and critical points of monodisperse PS samples in CH. In passing, we note that the unknown functions of T and P in eq 16 for J were all determined from light scattering data only. Nies et al. showed that the g function so established can describe fairly well the binodal data of Hashizume et al.[3] for the system f4 + f10 + CH. However, nothing is mentioned in their paper about the step that they must have taken to adapt eq 49 to this three-component system. Therefore, we are unable to make a detailed comparison between their approach and ours.

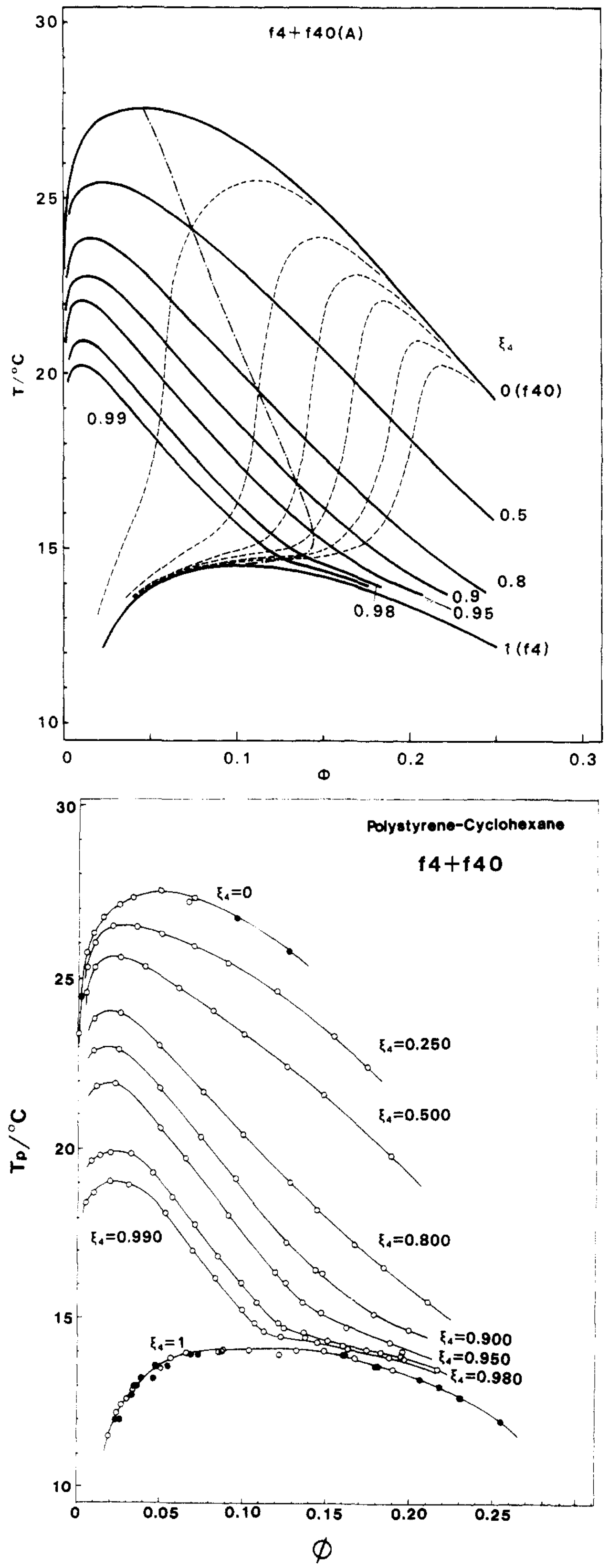

Figure 7. Cloud-point curves for system A for ξ_4 indicated: lower panel, experimental data (Tsuyumoto et al.[2]); upper panel, calculated results (solid lines, cloud-point curves; dashed lines, shadow curves; dot-dash line, locus of critical points).

Appendix

For a quasi-binary system we are unable to consider the special concentration that has been used to define the

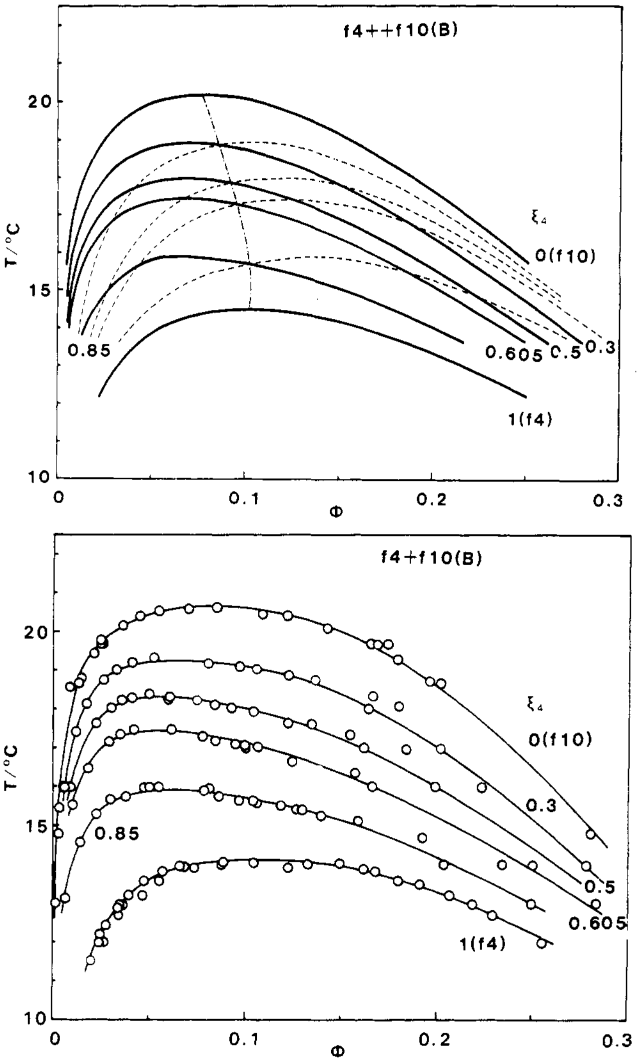

Figure 8. Cloud-point curves for system B for ξ_4 indicated: lower panel, experimental data (Hashizume et al.[3]); upper panel, calculated results (solid lines, cloud-point curves; dashed lines, shadow curves; dot-dash line, locus of critical points).

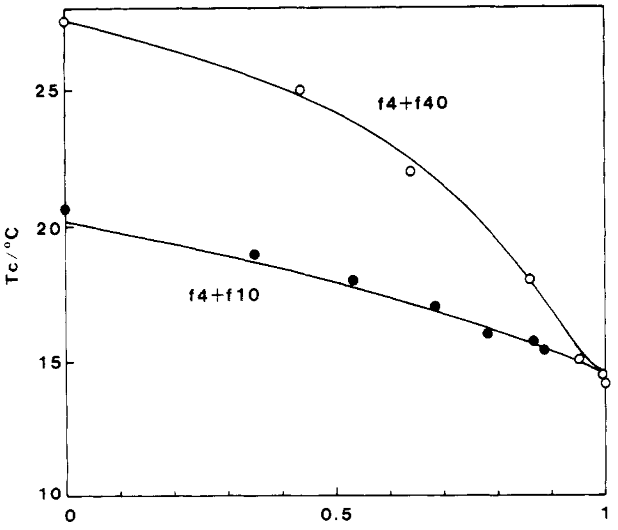

Figure 9. Critical temperature T_c as a function of ξ_4 for system A (unfilled circles) and system B (filled circles). Solid lines show calculated values.

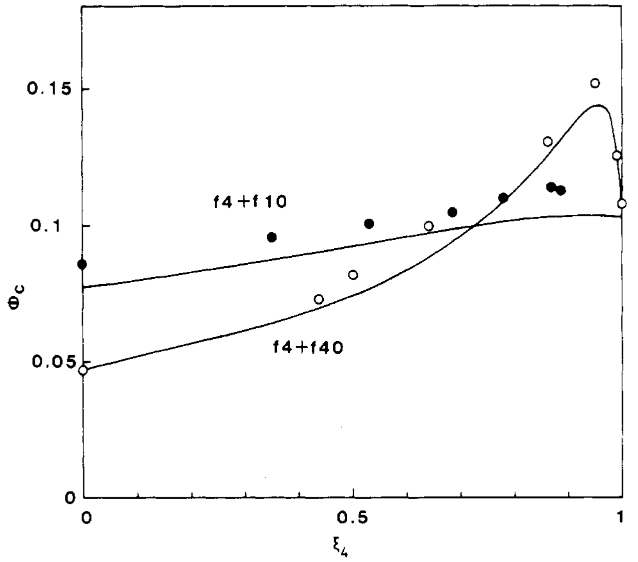

Figure 10. Critical volume fraction ϕ_c as a function of ξ_4 for system A (unfilled circles) and system B (filled circles). Solid lines show calculated values.

parameter b for a binary system since the volume fraction of segments in a polymer coil depends on the chain length. It is possible to define b for such a system in many ways.

For the ternary solution treated in the text we consider two hypothetical cases I and II. In I, polymer 2 is replaced by n_2P_2/P_1 pieces of polymer 1 chains, while, in II, polymer 1 is replaced by n_1P_1/P_2 pieces of polymer 2 chains. The volume fraction of total segments is the same for these hypothetical binary solutions. When the solution of case I is just filled with the covolumes of polymer coils, the volume fraction $\phi_1{}^h$ of the originally present polymer 1 chains, i.e., all chains in the solution minus those replacing polymer 2, is proportional to $n_1P_1/P_1{}^{3/2}[n_1 + (n_2P_2/P_1)]$ since, according to Koningsveld et al.,[4] each chain in the solution occupies a volume proportional to $P^{3/2}$. It can be readily seen that the proportionality factor is the parameter c defined in the text. Thus, we have

$$\phi_1{}^h = cn_1P_1{}^{1/2}/(n_1P_1 + n_2P_2) \tag{1'}$$

Similarly, we obtain

$$\phi_2{}^h = cn_2P_2{}^{1/2}/(n_1P_1 + n_2P_2) \tag{2'}$$

where $\phi_2{}^h$ is the volume fraction of the originally present polymer 2 chains in the solution of case II just filled with the covolumes of individual polymer coils.

If b for the ternary solution considered is defined as the sum of $\phi_1{}^h$ and $\phi_2{}^h$, it follows from eq 1′ and 2′ that

$$b = \xi b_1 + (1 - \xi)b_2 \tag{3'}$$

where $b_i = cP_i{}^{-1/2}$ represents b for a binary solution of polymer i. Equation 3′ expresses the assumption that we invoked in offering eq 39, i.e., the substitution (ii).

Registry No. Polystyrene (homopolymer), 9003-53-6; cyclohexane, 110-82-7.

References and Notes

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